Guidelines for

TPH Fractionation

at

Leaking Underground

Storage Tank Sites

prepared by the
Leaking Underground Storage Tank Program
Division of Environmental Response and Remediation
Utah Department of Environmental Quality

This document can be found on our Internet home page at:
http://www.eq.state.ut.us/eqerr/errhmpg.htm

FINAL DRAFT

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TABLE OF CONTENTS

INTRODUCTION:

This document is intended to provide the reader with a brief overview of Utah's Total Petroleum Hydrocarbons (TPH) Fractionation protocol used in conjunction with the risk-based corrective action (RBCA) program currently being implemented by the leaking underground storage tank (LUST) program. Sample preparation techniques that are to be used by the analytical laboratory in preparing an environmental sample for TPH fractionation analyses are described within Appendix A. Examples of standardized report formats to be used by analytical laboratories when reporting TPH Fractionation results are included within Appendix B.

SURROGATE SELECTION:

TPH fractionation is only required when a LUST site has been approved to conduct a risk assessment following RBCA protocols as outlined in "Guidelines for Utah's Corrective Action Process for Leaking Underground Storage Tank Sites" (July 30, 1999 - Second Edition Final Draft). These guidelines are available at: http://www.eq.state.ut.us/eqerr/errhmpg.htm. Figure 1 is a graphical illustration of Utah's TPH fractionation process to help the reader understand the relationship between EPA-promulgated analytical methods, and the chemical surrogates that are being used by Utah's LUST program for assigning specific toxicity values to the different TPH fractions.

In developing Utah's TPH fractionation process, staff evaluated existing protocols including those of the TPH criteria work group (TPHCWG), the Massachusetts Department of Environmental Protection (http://www.state.ma.us/dep/) and the Washington Department of Ecology (http://www.ecy.wa.gov/). In general, the fractionation approach involves resolving petroleum-based constituents into specific fractions or mass ranges based on similar chemical and physical fate and transport characteristics, and then assigning representative toxicity criteria to each fraction by using a specific chemical surrogate. Table 1 provides an overview of the different approaches used by these different agencies, including Utah's approach, in

SURROGATE SELECTION (Cont.):

deriving their TPH fractionation process and chemical surrogate selection for both the aromatic and aliphatic fractions of TPH. The purpose of this document is not to provide the reader with a comprehensive overview of the other programs and their approaches to this issue. Rather, this document provides a summary of the Utah-specific approach to the TPH fractionation and reporting process.

Table 2 outlines Utah's TPH fraction-specific and chemical-specific fate and transport properties and corresponding toxicity values (derived from the assigned chemical surrogates used by the LUST program). Table 3 describes how Utah's LUST program uses the values derived by the TPH fractionation process in determining appropriate site-specific cleanup levels for any given LUST site within the RBCA process.

For the reasons outlined herein, Utah chose a streamlined approach that would allow using existing analytical methods with only minimal changes to the way a laboratory would report results. Utah's preferred TPH fractionation method is based in-part on some of the following factors:

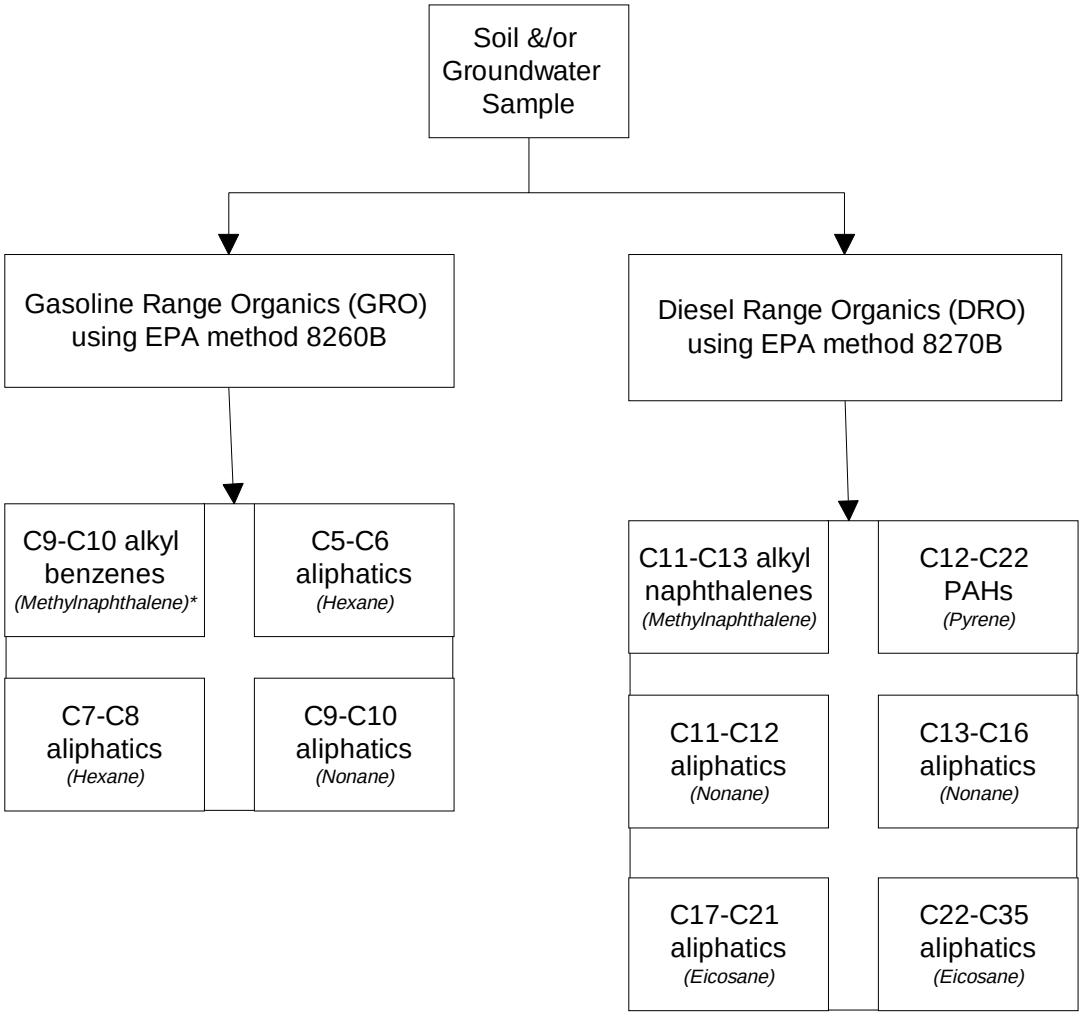
- Ability to use promulgated EPA methods already certified for use in Utah;
- Methods are readily available at commercial laboratories with no need for additional bench studies or reconfiguration of existing analytical hardware in the laboratory;
- Standardized analytical methods allow for consistent and reproducible results between different laboratories, sampling events and sampling locations; and,
- Cost is minimized for users since the laboratory is already set up to run the standardized method and only needs to accommodate the reporting format to report fractionation results.

Figure 1 shows the Utah-specific TPH fractionation groupings in relation to the corresponding analytical methods. Also shown are the specific surrogate chemicals used to represent the toxicity of each fraction. Some of the surrogates used (e.g., Pyrene, Hexane, Nonane and Eicosane) are the same as those used by other programs such as the Massachusetts Department of Environmental Protection in their VPH/EPH approach. Methylnaphthalene was selected as a surrogate for both the alkyl benzenes and the alkyl naphthalenes using an oral reference dose of 0.04 mg/Kg/day which best represents the different mass ranges and constituents of concern within these two aromatic fractions.

These guidelines are not meant to be inclusive of the entire LUST program, the RBCA process or the TPH fractionation protocol. As such, the reader of this document should call their state-assigned LUST project manager at (801) 536-4100 for answers to any site-specific questions they may have regarding the TPH fractionation protocol to ensure that they are using the TPH fractionation process correctly and in a cost-effective manner to minimize the need for unnecessary sampling at leaking underground storage tank sites.

FIGURE 1

Utah's Total Petroleum Hydrocarbon Fractionation & Analytical Method Relationship



* = Surrogate Chemical used for Toxicity values (RfD) in the RBCA Document.

Table 1: Comparison of TPH Fractionation Chemical Surrogates Used by Various Programs

Program/ Protocol	Aromatic Fraction	Aliphatic Fraction	EC #	Chemical or Toxicity Surrogate for Aromatics	Chemical or Toxicity Surrogate for Aliphatics	Analytical Method & Oral Reference Dose (mg/Kg/day) for Chemical Surrogate
TPHCWG	C6 - C7	C5 - C6	-	-	-	-
"	C7 - C8	C7 - C8	-	-	-	.2 for aromatics & 5.0 for aliphatics
"	C9 - C10	C9 - C10	-	-	-	.04 for aromatics & .1 for aliphatics
"	C11 - C12	C11 - C12	-	-	-	04 for aromatics & .1 for aliphatics
"	C13 - C16	C13 - C16	-	-	-	04 for aromatics & .1 for aliphatics
"	C17 - C21	C17 - C21	-	-	-	.03 for aromatics & 2.0 for aliphatics
"	C22 - C35	-	-	-	-	.03 for aromatics
WA DE TCP	C8 - C10 (PID) / EC = 9 (Trimethylbenzene)	C5 - C6 (FID) / EC = 5.5 (Hexane)	-	Biphenyl	cyclohexane	VPH / 5.7 for aliphatics & .05 for aromatics
"	C11 - C12 (PID) / EC = 11 (Naphthalene)	C7 - C8 (FID) / EC = 7 (Octane)	-	Biphenyl	cyclohexane	VPH / 5.7 for aliphatics & .05 for aromatics
"	-	C9 - C10 (FID) / Decane	9	-	-	VPH / .03 for aliphatics
"	-	C11 - C12 (FID) / Dodecane	11	-	-	VPH / .03 for aliphatics
"	C13 - C16 (acenaphthene)	C13 - C16 (Dodecane -hexadecane)	14	Biphenyl	-	EPH / .03 for aliphatics & .05 for aromatics
"	C17 - C21 (pyrene)	C17 - C21 (Hexadecane - Henicosane)	19	Pyrene	Mineral Oil	EPH / 2.0 for aliphatics & .03 for aromatics
"	C22 - C36 (benzoperylene)	C22 - C36 (Henicosane - Tetratricontane)	28	Pyrene	Mineral Oil	EPH / 2.0 for aliphatics & .03 for aromatics

Table 1 (Cont.): Comparison of TPH Fractionation Chemical Surrogates Used by Various Programs

Program/ Protocol	Aromatic Fraction	Aliphatic Fraction	EC#	Chemical or Toxicity Surrogate for Aromatics	Chemical or Toxicity Surrogate for Aliphatics	Analytical Method & Oral Reference Dose (mg/Kg/day) for Chemical Surrogate
MA DEP	C9 - C10	-	9	Pyrene	-	VPH / .03
“	C11 - C22	-	14	Pyrene	-	EPH / .03
“	-	C5 - C8	6	-	n-hexane	VPH / .06
“	-	C9 - C12	10	-	n-nonane	VPH / .6
“	-	C9 - C18	12	-	n-nonane	EPH / .6
“	-	C19 - C36	-	-	Eicosane	EPH / 6.0
Utah DEQ	C9 - C10 alkyl benzenes	-	-	Methylnaphthalene	-	8260B / .04
“	C11 - C13 alkyl naphthalenes	-	11	Methylnaphthalene	-	8270B / .04
“	C12 - C22 Polynuclear aromatic hydrocarbons (PAH’s)	-	16	Pyrene	-	8270B / .03
“	-	C5 - C6	6	-	Hexane	8260B / .06
“	-	C7 -C8	-	-	Hexane	8260B / .06
“	-	C9 - C10	9	-	Nonane	8260B / .1
“	-	C11 - C12	-	-	Nonane	8270B / .1
“	-	C13 - C16	-	-	Nonane	8270B / .1
“	-	C17 - C21	20	-	Eicosane	8270B / 2.0
“	-	C22 - C35	-	-	Eicosane	8270B / 2.0

Table 2: TPH Fraction-Specific [a] and Chemical-Specific Property [a] and Toxicity Values

TPH Fractions and Chemicals showing Carbon Number and Representative CAS number	EPA Analy-tical Method [b]	Mole-cular Weight (g/mol)	Vapor Pressure [c] (mm Hg)	Henry's Law Constant [d] ($L\text{-}H_2O$/ L-air, unitless)	Diffusion Coefficient in Air [e] (D^{air}, cm^2/s)	Diffusion Coefficient in Water [e] (D^w, cm^2/s)	Aqueous Solubility (20-25° C) (pure compound) (mg/L)	Adsorption Coefficient (Koc) (mL/g)	Cancer Slope Factor, Oral (SF_o) (kg-day/mg)	Cancer Slope Factor, Inhalation (SF_i) (kg-day/mg)	Reference Dose, Oral (RfD_o) (mg/kg-day)	Reference Dose, Inhalation [f] (RfD_i) (mg/kg-day)
ALIPHATICS												
C_5 - C_6 110-54-3	8260B	81	2.66 E+02 [g]	4.10 E+01	8.57 E-02	8.34 E-06	3.60 E+01	6.31 E+02	-	-	6.00 E-02 [h]	6.00 E-02 [h]
C_7 - C_8 142-82-5	8260B	100	4.80 E+01	7.70 E+01	6.69 E-02	6.89 E-06	5.40 E+00	3.16 E+03	-	-	6.00 E-02 [h]	6.00 E-02 [h]
C_9 - C_{10} 111-84-2	8260B	130	5.00 E+00	1.60 E+02	6.44 E-02	5.90 E-06	4.30 E-01	3.16 E+04	-	-	1.00 E-01 [i]	2.90 E-01 [i]
C_{11} - C_{12} 1120-21-4	8270B	160	4.80 E-01	1.60 E+02	4.60 E-02	5.19 E-06	3.40 E-02	3.16 E+05	-	-	1.00 E-01 [i]	2.90 E-01 [i]
C_{13} - C_{16} 544-76-3	8270B	200	3.60 E-02	1.60 E+02	3.95 E-02	4.50 E-06	7.60 E-04	5.00 E+06	-	-	1.00 E-01 [i]	2.90 E-01 [i]
C_{17} - C_{21} 544-76-3	8270B	270	8.40 E-04	1.10 E+02	3.28 E-02	3.76 E-06	2.50 E-06	4.00 E+08	-	-	2.00 E+00 [i]	na [i]
C_{22} - C_{35} 629-78-7	8270B	280	8.40 E-04	1.10 E+02	3.28 E-02	3.76 E-06	1.50 E-06	4.00 E+08	-	-	2.00 E+00 [i]	na [i]

Table 2 (Cont.): TPH Fraction-Specific [a] and Chemical-Specific [a] Property and Toxicity Values

TPH Fractions and Chemicals showing Carbon Number and Representative CAS number	EPA Analytical Method [b]	Molecular Weight (g/mol)	Vapor Pressure [c] (mm Hg)	Henry's Law Constant [d] ($L\text{-}H_2O$/ L-air, unitless)	Diffusion Coefficient in Air [e] (D^{air}, cm^2/s)	Diffusion Coefficient in Water [e] (D^w, cm^2/s)	Aqueous Solubility (20-25° C) (pure compound) (mg/L)	Adsorption Coefficient (Koc) (mL/g)	Cancer Slope Factor, Oral (SF_o) (kg-day/mg)	Cancer Slope Factor, Inhalation (SF_i) (kg-day/mg)	Reference Dose, Oral (RfD_o) (mg/kg-day)	Reference Dose, Inhalation[f] (RfD_i) (mg/kg-day)
AROMATICS												
Benzene C_6 71-43-2	8260B	78.11	9.50 E+01	2.25 E-01	8.80 E-02	9.80 E-06	1.78 E+03	8.12 E+01	2.90 E-02 [j]	2.90 E-02 [j]	-	-
Toluene C_7 108-88-3	8260B	92.13	2.85 E+01	2.74 E-01	8.57 E-02	8.60 E-06	5.15 E+02	2.34 E+02	-	-	2.00 E-01 [j]	1.10 E-01 [j]
Ethylbenzene C_8 100-41-4	8260B	106.2	9.50 E+00	3.58 E-01	7.50 E-02	7.80 E-06	1.52 E+02	5.37 E+02	-	-	1.00 E-01 [j]	2.90 E-01 [j]
Xylenes C_8 1330-20-7 [l]	8260B	106.2	8.59 E+00	2.52 E-01	7.85 E-02	8.90 E-06	1.98 E+02	5.86 E+02	-	-	2.00 E+00 [j]	2.00 E+00 [j]
Naphthalene C_{10} 91-20-3	8260B	128.19	2.76 E-01	1.74 E-02	5.90 E-02	7.50 E-06	3.10 E+01	8.44 E+02	-	-	2.00 E-02 [k]	8.60 E-04 [k]
Methyl t-Butyl Ether (MtBE) 1634-04-4 [m]	8260B	88.146	2.49 E+02	2.40 E-02	7.92 E-02	9.41 E-05	4.30 E+04	1.20 E+01	-		5.00 E-03 [o]	8.57 E-01 [k]
C_9 - C_{10} (alkyl benzenes) 108-67-8	8260B	120.2 - 134.22	5.00 E+00	4.20 E-01	6.00 E-02	7.51 E-06	1.10 E+02	1.26 E+03	-	-	4.00 E-02 [i]	6.00 E-02 [i]
C_{11} - C_{13} (total alkyl naphthalenes) [n] 90-12--0	8270B	142.2 - 176.2	5.00 E-02	2.30 E-02	4.80 E-02	7.67 E-06	1.45 E+03	7.06 E+03	-	-	4.00 E-02 [i]	6.00 E-02 [i]
C_{12} - C_{22} [p] (polynuclear aromatic hydrocarbons) 56-55-3	8270B	152.21 - 278.35	2.70 E-03	4.12 E-01	3.23 E-02	1.66 E-05	4.86 E+01	6.29 E+04	-	-	3.00 E-02 [i]	na [i]

Table 2 (Cont.): TPH Fraction-Specific [a] and Chemical-Specific [a] Property and Toxicity Values

TPH Fractions and Chemicals showing Carbon Number and Representative CAS number	EPA Analytical Method [b]	Molecular Weight (g/mol)	Vapor Pressure [c] (mm Hg)	Henry's Law Constant [d] ($L\text{-}H_2O$/ L-air, unitless)	Diffusion Coefficient in Air [e] (D^{air}, cm^2/s)	Diffusion Coefficient in Water [e] (D^w, cm^2/s)	Aqueous Solubility (20-25° C) (pure compound) (mg/L)	Adsorption Coefficient (Koc) (mL/g)	Cancer Slope Factor, Oral (SF_o) (kg-day/mg)	Cancer Slope Factor, Inhalation (SF_i) (kg-day/mg)	Reference Dose, Oral (RfD_o) (mg/kg-day)	Reference Dose, Inhalation[f] (RfD_i) (mg/kg-day)
POLYNUCLUEAR AROMATIC HYDROCARBONS (PAHs)												
Acenaphthylene C_{12} 208-96-8	8270B	152.2	3.11 E-02	3.39 E-03	4.40 E-02	7.53 E-06	1.61 E+01	2.77 E+03	-	-	3.00 E-02 [q]	na
Acenaphthene C_{12} 83-32-9	8270B	154.21	1.14 E-02	4.91 E-03	4.21 E-02	7.69 E-06	3.80 E+00	2.38 E+03	-	-	6.00 E-02 [j]	1.70 E-02 [i]
Fluorene C_{13} 86-73-7	8270B	166.2	5.37 E-03	3.19 E-03	3.60 E-02	7.88 E-06	1.90 E+00	3.90 E+03	-	-	4.00 E-02 [j]	1.10 E-02 [i]
Phenanthrene C_{14} 85-01-8	8270B	178.2	8.51 E-40	1.31 E-03	3.30 E-02	7.47 E-06	1.10 E+00	8.14 E+03	-	-	3.00 E-02 [q]	na
Anthracene C_{14} 120-12-7	8270B	178.2	5.84 E-04	1.60 E-03	3.24 E-02	7.74 E-06	4.50 E-02	7.69 E+03	-	-	3.00 E-01 [j]	8.57 E-02 [i]
Fluoranthene C_{16} 206-44-0	8270B	202.3	6.54 E-05	4.17 E-04	3.02 E-02	6.35 E-06	2.60 E-01	2.78 E+04	-		4.00 E-02 [j]	1.14 E-02 [i]
Pyrene C_{16} 129-00-0	8270B	202.3	8.89 E-05	3.71 E-04	2.70 E-02	7.24 E-06	1.32 E-01	2.57 E+04	-	-	3.00 E-02 [j]	8.57 E-03 [i]
Benz(a)-Anthracene C_{18} 56-55-3	8270B	228.3	4.54 E-06	2.34 E-04	5.10 E-02	9.00 E-06	1.10 E-01	1.02 E+05	7.30 E-01 [i]	7.30 E-02 [i]	-	-

Table 2 (Cont.): TPH Fraction-Specific [a] and Chemical-Specific [a] Property and Toxicity Values

TPH Fractions and Chemicals showing Carbon Number and Representative CAS number	EPA Analytical Method [b]	Molecular Weight (g/mol)	Vapor Pressure [c] (mm Hg)	Henry's Law Constant [d] ($L\text{-}H_2O$/ L-air, unitless)	Diffusion Coefficient in Air [e] (D^{air}, cm^2/s)	Diffusion Coefficient in Water [e] (D^w, cm^2/s)	Aqueous Solubility (20-25° C) (pure compound) (mg/L)	Adsorption Coefficient (Koc) (mL/g)	Cancer Slope Factor, Oral (SF_o) (kg-day/mg)	Cancer Slope Factor, Inhalation (SF_i) (kg-day/mg)	Reference Dose, Oral (RfD_o) (mg/kg-day)	Reference Dose, Inhalation [f] (RfD_i) (mg/kg-day)
POLYNUCLEAR AROMATIC HYDROCARBONS (PAHs), continued												
Chrysene C_{18} 218-01-9	8270B	228.3	8.06 E-07	1.80 E-04	2.48 E-02	6.21 E-06	1.50 E-03	8.14 E+04	7.30 E-03 [i]	7.30 E-03 [i]	-	-
Benzo(b)-Fluoranthene C_{20} 205-99-2	8270B	252.32	5.07 E-05	8.36 E-04	2.26 E-02	5.56 E-06	1.50 E-03	8.30 E+04	7.30 E-01 [i]	7.30 E-01 [i]	-	-
Benzo(k)-Fluoranthene C_{20} 207-08-9	8270B	252.32	3.09 E-08	6.46 E-06	2.26 E-02	5.56 E-06	8.00 E-04	1.21 E+05	7.30 E-02 [i]-	7.30 E-02 [i]	-	-
Benzo(a)-Pyrene C_{20} 50-32-8	8270B	252.3	1.60 E-07	1.86 E-05	4.30 E-02	9.00 E-06	3.80 E-03	1.31 E+05	7.30E+00 [m]-	6.10E+00 [m]-	-	-
Indeno(1, 2, 3-Cd) Pyrene C_{22} 193-39-5	8270B	276.34	7.60 E-07	2.07 E-11	2.30 E-02	4.41 E-06	6.20 E-02	8.00 E+05	7.30 E-01 [o]	6.10 E-01 [o]	-	-
Dibenzo-(a, h) Anthracene C_{22} 53-70-3	8270B	278.35	5.20 E-10	1.58 E-05	2.00 E-02	5.24 E-06	5.00 E-04	7.41 E+05	7.30 E-01 [o]	6.10 E-01 [o]	-	-
Benzo(g, h, i)-Perylene C_{20} 191-24-2	8270B	268.36	1.69 E-07	3.03 E-05	4.90 E-02	5.56 E-06	3.00 E-04	3.11 E+05	-	-	3.00 E-02 [q]	na [q]

Table 2 (Cont.): TPH Fraction-Specific [a] and Chemical-Specific [a] Property and Toxicity Values

Notes: - not applicable
na not available

[a] after Gustafson, et. al., 1997, Tables 3, 7 and 8.

[b] The EPA laboratory methods listed only pertain to the TPH fractionation process. Note that MTBE/BTEXN are also analyzed and reported when using EPA method 8260B for the TPH fractionation.

[c] mm Hg = 760 X atmospheres

[d] Henry's Law Constant (H) unit conversion:

$$\frac{H\ unitless}{41.6} = \frac{H\ atmospheres \times meter^3}{mole}$$

[e] Diffusion coefficients for the TPH fractions are based on averages shown in Gustafson, et al., 1997, Table 3.

[f] Conversion formula for converting Reference Concentration (RfC) mg/m^3 to Reference Dose-inhalation (RfD_i) mg/kg-day:

$$RfC\ \frac{mg}{m^3} \times \frac{1}{70\ kg\ body\ weight} \times \frac{20m^3}{day}\ breathing\ rate = RfD_i\ \frac{mg}{kg\text{-}day}$$

[g] E = Exponent to the base 10; for example, 7.45 E-05 = $7.45 \times 10^{-5} = 0.0000745$

[h] Hexane RfD and RfC based on USEPA (HEAST), 1997.

[i] after Edwards, et al., 1997.

[j] USEPA (IRIS), 1998a.

[k] USEPA (IRIS), 1998b.

[l] Total xylenes parameter values are based on average values of ortho-xylene, para-xylene and meta-xylene.

[m] ASTM, 1997.

[n] C_{11} - C_{13} alkyl (or methyl) naphthalenes include the following chemicals. Fate and transport properties for this fraction are based on average values:

2-Methyl-naphthalene C_{11}
1-Methyl-naphthalene C_{11}
Total Dimethyl Naphthalenes C_{12}
Total Trimethyl Naphthalenes C_{13}

[o] USEPA Region 3 Risk-Based Concentration table, EPA Region 3, March 1995.

[p] C_{12} - C_{22} polynuclear aromatic hydrocarbons include the following chemicals. Fate and transport properties for this fraction are based on average values:

Acenaphthylene	C_{12}
Acenaphthene	C_{12}
Fluorene	C_{13}
Phenanthrene	C_{14}
Anthracene	C_{14}
Fluoranthene	C_{16}
Pyrene	C_{16}
* Benz(a)-Anthracene	C_{18}
* Chrysene	C_{18}
* Benzo(b)-Fluoranthene	C_{20}
* Benzo(k)-Fluoranthene	C_{20}
* Benzo(a)-Pyrene	C_{20}
* Indeno(1,2,3-Cd)Pyrene	C_{22}
* Dibenzo(a,h)Anthracene	C_{22}
Benzo(g,h,i)Perylene	C_{22}

* = Carcinogenic compounds. If these compounds are detected, SSCLs must be calculated for those compounds using their unique chemical and toxicity parameter values.

[q] no toxicity data available; values used are for the C_{17} to C_{35} aromatic fraction according to Edwards, et al., 1997.

Table 3: Determination of RBSL and SSCL Values for Total Petroleum Hydrocarbons (TPH)

1. Sample Collection

- Collect a minimum of one environmental sample which is representative of each contaminated medium (e.g., soil and groundwater) and the maximum concentration and composition of the petroleum contamination at the site. For sites where TPH contamination is highly variable in concentration or composition, the user should collect multiple TPH samples at representative locations to ensure a representative analysis by the laboratory.

2. Laboratory Analysis

- Analyze the sample(s) using EPA methods 8260B and 8270B. Specify "Utah TPH Fractionation" on your chain of custody forms to ensure that the laboratory uses the reporting format specific for TPH fractionation which differs from a typical 8260B and/or 8270B chemical parameter listing. The laboratory should report concentrations for each of the 10 different TPH fractions listed in Table 2. In addition, on the 8260B report, the laboratory should list values for any detectable BTEXN and MTBE. For fractions where the measured concentration is below the method reporting limit, a value of half the method reporting limit should be used as the representative source area concentration in deriving SSCLs.

3. Determination of Tier 2 RBSLs for Each TPH Fraction

- Fraction-specific RBSL values must be derived for each complete exposure pathway at the site. For each TPH fraction, RBSL values can be calculated for each relevant exposure pathway using the equations provided on Table C-1 (see Equations C.1 through C.8). Fraction-specific chemical property values and toxicological parameters to be used in the RBSL calculations are provided in Table 2.

4. Determination of SSCL Values for TPH Fractions

- Under Tier 2 Options 2 through 4, SSCL values for the individual TPH fractions are developed in the same manner as for any other COCs (e.g., BTEXN and MTBE). Using the chemical property values and toxicological parameter values listed on Table 2, a NAF value may be derived for each TPH fraction using the Option 2 through 4 calculation methods. The NAF is then multiplied by the appropriate RBSL value to obtain an SSCL for each complete exposure pathway. The fraction that exceeds it's applicable SSCL the most will ultimately drive the cleanup for all the other fractions contained within TPH at the site.

5. Confirmation Sampling for TPH Fractions Following TPH-Driven Cleanup Activities

- After completing cleanup activities that are driven by the exceedence of SSCLs for the TPH fraction(s), the user should obtain an appropriate number of environmental samples at representative locations and depths in order to verify the effectiveness of the cleanup at the release site. The same procedures described herein would again be employed for comparison with representative source area TPH fractionation values obtained. During cleanup, the user may elect to obtain samples for TPH fractionation, and BTEXN and MTBE (8260B method) if applicable, to measure the relative progress of the cleanup activities and to estimate the cleanup duration.

APPENDIX A

TPH Fractionation

Sample Preparation Guidelines

for Analytical Laboratories

TPH Fractionation Extraction Method (SW 3510B Modified)

1.0 Scope

1.1 Extraction of Semi-Volatile petroleum compounds.
1.2 References - EPA method 3510 B, Revision 2, September 1994 and 8270.

2.0 Summary

2.1 The purpose of this procedure is to provide guidance and instruction in the execution of EPA method 3510 B and its modifications in the extraction of petroleum products.

3.0 Interference's

3.1 Refer to EPA method 3510B.

4.0 Equipment and Apparatus

4.1 Two Liter separatory funnel with Teflon stopcock.
4.2 pH paper, 1-14 range
4.3 Syringes: 1000ul
4.4 200 ml Turbo Vap tube
4.5 Graduated Cylinder, 1000 ml
4.6 Drying funnels
4.7 Glass wool
4.8 Solvent dispenser

5.0 Reagents

5.1 Sodium Sulfate:
5.2 Solvents: Methylene Chloride pesticide grade.
5.3 DI water
5.4 $NaOH/H_2SO_4$

6.0 Sample preservation and Holding

6.1 Samples should be refrigerated at 4 degrees C. Holding times are 14 days for waters.
6.2 Samples should be brought to room temperature before extracting.

7.0 Extraction

7.1 Set up drying funnels with glass wool containing approximately 10g Sodium Sulfate. Rinse the Sodium Sulfate with 20-25ml Methylene Chloride, discarding the solvent.
7.2 Rinse all remaining glassware with methylene chloride and then discard solvent. Remove surrogates and spikes from refrigerator and allow to come to room temperature.

7.3 Turn the extraction heaters on. Measure 500ml of sample into a clean 2 liter separatory funnel (if sample volume is <500ml, bring total volume to 500ml using DI water). Record initial volume on extraction report. Repeat for MS and MSD. For the method blanks and LCS add 500 ml of DI water to clean 2 liter separatory funnel.

7.4 Check and record the initial pH. Adjust the pH to between 7 and 9 with 60% $NaOH/H_2SO_4$ solution.

7.5 Add 500 ul Surrogate spike solution to each sample, blank, LCS, MS, MSD.

7.6 Add 500 ul Matrix Spiking Solution to LCS, MS, and MSD.

7.7 Add 35 ml methylene chloride to the separatory funnel. Seal and shake the separatory funnel for 2-3 minutes, venting frequently.

7.8 Allow the methylene chloride and sample to separate for 10 minutes.

7.8.1 If an emulsion results that is greater than 1/3 the solvent layer, it must be broken up prior to the draining of the methylene chloride.

7.8.2 Stir with a pipette until emulsion layer is broken up. Other separation techniques might include a slow drain, decanting methylene chloride into beaker and returning emulsion to sep funnel, or centrifuging.

7.8.3 Drain the entire emulsion into as many clean 40 ml screw cap vials as necessary. Cap the vitals, label and place in centrifuge. Spin at 30-35 r.p.m. for a 2 to 5 minutes, or until layers separate. Using a pipette, remove methylene chloride from 40 ml vial. Return emulsion layer to sep funnel followed by a rinse of methylene chloride.

7.9 Decant solvent through drying funnel, into pre-rinsed Turbo Vap tube being sure to rinse the sodium sulfate with approximately 25 ml clean methylene chloride following the last pour.

7.10 Repeat steps 7.7 through 7.9 two more times.

7.11 Place the Turbo Vap tube in Turbo Vap at 35°C with 12 p.s.i. ultra high purity nitrogen.

7.12 Concentrate extract to 0.5 ml and transfer to GC vial. Extract is now ready for analysis.

8.0 Quality Control

8.1 Each group of samples should be extracted with a Method Blank, Laboratory Control Sample (LCS), Matrix Spike (MS), and Matrix Spike Duplicate (MSD). Each sample batch should contain no more than 20 samples. If insufficient sample is provided to perform the proper QC, (MS, MSD), a Laboratory Control Sample Duplicate (LCSD) may be performed in their place. All QC samples must go through the same extraction steps as the samples.

9.0 Safety

9.1 Eye protection must be worn at all times.

9.2 Non-Latex, nitrile exam gloves must be worn at all times when performing extractions.

9.3 Lab coats must be worn at all times when performing extractions.

1.0 Scope

1.1 The purpose of this procedure is to provide guidance and instruction in the execution of EPA Method 3550A (ultrasonic extraction of soils sludge's and waste). This procedure is for solid samples only.

2.0 Apparatus and Material

2.1 Mortal, pestle and hammer for grinding dry waste samples.
2.2 Wrist action shaker
2.3 Drying oven aluminum crucible.
2.4 Beakers
2.5 Turbo Vap concentrator & 200 ml Turbo Vap tubes.
2.6 Funnels
2.7 Balance capable of measuring accurately to .001 g
2.8 GC Vitals, 2 ml with aluminum seal cap
2.9 Stainless steel spatula
2.10 Syringes 1000 ul.
2.11 Whatman No. 41 filter paper.

3.0 Reagents

3.1 Sodium sulfate (granular, anhydrous), Na2SO4. Purify by heating at 400°C for 4 hours in a shallow pan (if not done by the manufacturer).
3.2 Methylene chloride, pesticide quality or equivalent

4.0 Sample preservation and handling

4.1 Samples should be refrigerated at 4°C. Holding time is 14 days from the sampling date.
4.2 Samples are to be brought to room temperature before extracting.

5.0 Preliminary Evaluation

5.1 Rinse all glassware with methylene chloride. If water is present, rinse first with isopropyl alcohol then rinse with methylene chloride.
5.2 Remove surrogates and spikes from freezer and allow to come to room temperature.
5.3 Percent moisture determination: Decant and discard any water layer. Mix thoroughly. Determine the dry weight of the sample by weighing out 5-10 g of sample into a tarred crucible. Dry over night at 105°C. Cool in a desiccator.

$$\% \text{ moisture} = \frac{\text{gram of sample - gram of dry sample}}{\text{initial sample in grams}} * 100$$

5.4 Prepare multi-phasic samples by the phase separation method described in chapter 2 of SW-846.

6.0 Low level extraction

6.1 Turn extraction heaters on. Set up evaporator flasks and concentrator tubes. Place a funnel with filter paper (Whatman No. 41) containing approximately 10 grams sodium sulfate on top of concentrator apparatus. Rinse sodium sulfate and Turbo Vap tubes with approximately 25 ml clean methylene chloride and discard solvent.

6.2 Weigh 15.0 $\pm$ .lg of sample into a clean 40 ml VOA vile. Nonporous or wet samples that do not have a free flowing sandy texture must be mixed with 15 g of anhydrous sodium sulfate using a spatula. More sodium sulfate may be added if necessary until the sample is free flowing. For blanks and Laboratory Control Samples (LCS), add 15.0 g $\pm$ .l g anhydrous sodium sulfate to clean 40 ml VOA vial.

6.3 Add surrogates such that the final concentration is 100 ug/ml.

6.4 Add Matrix spike stock solution to the MS and MSD and LCS such that the final concentration is 100 ug/ml.

6.5 Add 25 ml methylene chloride to each sample making sure that each sample is sufficiently covered with solvent.

6.6 Shake sample for 3 minutes on a wrist action shaker.

6.7 Decant Solvent through drying column into Turbo Vap tube.

6.8 Repeat steps 6.5 through 6.7 one more time.

6.9 Place the Turbo Vap tube in Turbo Vap at 35ºC with 12 p.s.i. ultra high purity nitrogen.

6.10 Concentrate extract to 0.5 ml and transfer to GC vial. Extract is now ready for analysis.

7.0 Quality Control

7.1 Each group of samples should be extracted with a Method Blank, Laboratory Control Sample (LCS), Matrix Spike (MS), and Matrix Spike Duplicate (MSD). Each sample batch should contain no more than 20 samples. If insufficient sample is provided to perform the proper QC, (MS, MSD), a Laboratory Control Sample Duplicate (LCSD) may be performed in their place. All QC samples must go through the same extraction steps as the samples.

8.0 Safety

8.1 Eye protection must be worn at all times.

8.2 Non-latex, nitrile exam gloves must be worn at all times when performing extractions.

8.3 Lab coats must be worn at all times when performing extractions.

APPENDIX B

Standard Reporting Format

for

TPH Fractionation

ORGANIC ANALYSIS REPORT

Client: Contact:
Date Sampled: Date Received:

Lab Set ID: Received by:

Analysis Requested:	Analysis Method:	Date Analyzed:
Utah TPH Fractionation	EPA SW-846 #8260B Sample Prep: 5030A	

Lab Sample ID:	Field Sample ID:	Reporting Units:
		ppb (ug/L)

Analytical Results Volatile Fractionation

Compound:	Reporting Limit:	Amount Detected:
Methyl tert-butyl ether	2	<2
Benzene	1	<1
Toluene	2	<2
Ethylbenzene	2	<2
Total Xylenes	2	<2
Naphthalene	4	<4
C9 & C10 Alkyl Benzenes	2	<2
C5 & C6 Aliphatic hydrocarbons	20	<20
C7 & C8 Aliphatic hydrocarbons	20	<20
C9 & C10 Aliphatic hydrocarbons	20	<20

Surrogate QA/QC	% Recovery	QC Limits

Footnotes:
Dilution Factor = 1.0

Approved by: _____ Date:_____
Laboratory Supervisor

ORGANIC ANALYSIS REPORT

Client: Contact:
Date Sampled: Date Received:
Lab Set ID: Received by:

Analysis Requested:	Analysis Method:	Date Analyzed:
Utah TPH Fractionation	EPA SW-846 #8270B Sample Prep: 3510B	

Lab Sample ID:	Field Sample ID:	Reporting Units:
		ppb (ug/L)

Analytical Results Semi-Volatile Fractionation

Compound:	Reporting Limit:	Amount Detected:
Acenaphthylene	15	<15
Acenaphtene	15	<15
Fluorene	15	<15
Phenanthrene	15	<15
Anthracene	15	<15
Fluoranthene	15	<15
Pyrene	15	<15
Benz(a)Anthracene	15	<15
Chrysene	15	<15
Benzo(b)Fluoranthene	15	<15
Benzo(k)Fluoranthene	15	<15
Benzo(a)Pyrene	15	<15
Ideno(1,2,3-Cd)Pyrene	15	<15
Dibenz(a,h)Anthracene	15	<15
Benzo(g,h,i)Perylene	15	<15
C12 to C22 Total PAHs*	25	<25
C11 to C12 Aliphatic hydrocarbons	25	<25
C13 to C16 Aliphatic hydrocarbons	25	<25
C17 to C21 Aliphatic hydrocarbons	25	<25
C22 to C35 Aliphatic hydrocarbons	25	<25
C11 to C13 Alkyl Naphthalenes**	25	<25

Surrogate QA/QC	% Recovery	QC Limits

Footnotes:

* This value is a summation of the above-listed compounds

** This value is a summation of total methyl, di-methyl and tri-methyl naphthalene isomers

Approved by: _____ Date:_____

Laboratory Supervisor

ORGANIC ANALYSIS REPORT

Client:	Contact:
Date Sampled:	Date Received:
Lab Set ID:	Received by:

Analysis Requested:	Analysis Method:	Date Analyzed:
Utah TPH Fractionation	EPA SW-846 #8260B	

Sample Prep: 5030A

Lab Sample ID: Field Sample ID: Reporting Units: ppb (ug/Kg)

Analytical Results Semi-Volatile Fractionation

Compound:	Reporting Limit:	Amount Detected:
Methyl tert-butyl ether	2	<2
Benzene	1	<1
Toluene	2	<2
Ethylbenzene	2	<2
Total Xylenes	2	<2
Naphthalene	4	<4
C9 & C10 Alkyl Benzenes	2	<2
C5 & C6 Aliphatic hydrocarbons	20	<20
C7 & C8 Aliphatic hydrocarbons	20	<20
C9 & C10 Aliphatic hydrocarbons	20	<20

Surrogate QA/QC	% Recovery	QC Limits

Footnotes:
Dilution Factor = 1.0

Approved by: _____ Date:_____
Laboratory Supervisor

ORGANIC ANALYSIS REPORT

Client:
Date Sampled:
Lab Set ID:

Contact:
Date Received:
Received by:

Analysis Requested:
Utah TPH Fractionation

Analysis Method:
EPA SW-846 #8270B
Sample Prep: 3550A

Date Analyzed:

Lab Sample ID:

Field Sample ID:

Reporting Units:
ppb (ug/Kg)

Analytical Results Semi-Volatile Fractionation

Compound:	Reporting Limit:	Amount Detected:
Acenaphthylene	15	<15
Acenaphtene	15	<15
Fluorene	15	<15
Phenanthrene	15	<15
Anthracene	15	<15
Fluoranthene	15	<15
Pyrene	15	<15
Benz(a)Anthracene	15	<15
Chrysene	15	<15
Benzo(b)Fluoranthene	15	<15
Benzo(k)Fluoranthene	15	<15
Benzo(a)Pyrene	15	<15
Ideno(1,2,3-Cd)Pyrene	15	<15
Dibenz(a,h)Anthracene	15	<15
Benzo(g,h,i)Perylene	15	<15
C12 to C22 Total PAHs*	25	<25
C11 to C12 Aliphatic hydrocarbons	25	<25
C13 to C16 Aliphatic hydrocarbons	25	<25
C17 to C21 Aliphatic hydrocarbons	25	<25
C22 to C35 Aliphatic hydrocarbons	25	<25
C11 to C13 Alkyl Naphthalenes**	25	<25

Surrogate QA/QC	% Recovery	QC Limits

Footnotes:

* This value is a summation of the above-listed compounds

** This value is a summation of total methyl, di-methyl and tri-methyl naphthalene isomers

Approved by: _____ Date:_____

Laboratory Supervisor